AMENDED SPECIFICATION

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PATENT SPECIFICATION

NO DRAWINGS

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811,820

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COMPLETE SPECIFICATION

Catalytic Hydrogenation of Acetylene

SPECIFICATION NO. 811,820

By a direction given under Section 17 (1) of the Patents Act 1949 this application proceeded in the name of Engelhard Industries, Inc., a corporation organised and existing under the laws of the State of Delaware, United States of America, of 113, Astor Street, Newark 2, New Jersey, United States of America.

THE PATENT OFFICE,
12th May, 1961

DS 92137/1(1)/R.153 200 5/61 PL

lytic hydrogenation of acetylene wherein the acetylene is present in a mixture with other gases, and is more particularly concerned with the purification of gaseous mixtures from small amounts of acetylene.

Palladium has been used as a catalyst in the direct hydrogenation of acetylene to ethylene by adding an excess of hydrogen. In one such process of direct hydrogenation acetylene together with an excess of hydrogen and steam was passed over a catalyst of palladium on silica gel at temperatures of about 200° C. to 300° C. and under normal pressures. The palladium in such a catalyst is usually present in great dispersion on the silica gel, e.g. 200 mg per liter. Such catalysts however, have been found to become poisoned quickly due to the presence of organic compounds of P, As, Sb and the hydrides of P, As, and Sb, organic compounds of S, H_2S, HCN, and polymerizing compounds such as vinyl acetylene. Such a catalyst shows a tendency to over-hydrogenate and produces tars, cuprene, polymers and other undesirable by-products. As high as 30 to 40% of organic matter has been found in such catalysts. Thus, repeated regeneration is

There is thus a need for a catalyst capable of selectively hydrogenating acetylene in the presence of other gases, particularly olefines, wherein the acetylene content must be effectively eliminated or reduced to only tiny amounts, and not more than 1% of any ethylene present is converted to ethane.

It is therefore one object of the present invention to provide a catalytic process for the hydrogenation of the triple bond of acetylene. It is a further object of the invention to provide a catalytic process for the selective hydrogenation of even traces of acetylene to ethylene when the acetylene is present in a mixture with saturated and unsaturated gases. A still further object is to provide a simple and economical catalytic process for the selective hydrogenation of acetylene to ethylene when the acetylene is present in traces in a mixture with olefines. Other objects and advantages of the invention will become readily apparent from the following description.

We, have now determined that selective hydrogenation of acetylene, wherein the acetylene is present in a mixture with other

Catalytic hydrogenation of acetylene

Description of **GB811820**

COMPLETE SPECIFICATION
Catalytic Hydrogenation of Acetylene
We, ENGLEHARD INDUSTRIES, INC., formerly
Baker & Company Incorporated, of 113 Astor
Street, Newark, New Jersey,Unired States of
America, a corporation organized under the laws of the State of New Jersey, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the followingstatement:
'This invention relares to the selective catalytic hydrogenationof acetylene wherein the acetylene is present in a mixture with other gases, and is more particularly concerned with the purification of gaseous mixtures from small amounts of acetylene.

Palladium has been used as a catalyst in the direct hydrogenation of acetylene to ethylene by adding an excess of hydrogen. In one such process of direct hydrogenarion acetylene together with an excess of hydrogen and steam was passed over a catalyst of palladium on silica gel at temperatures of about 2000 C. to300 C. and under normal pressures. The palladium in such a catalyst is usually present in great dispersion on the silica gel, e.g. 200 mg per liter. Such catalysts however, have been found to become poisoned quickly due to the presence of organic compounds of P, As,
Sb and the hydrides of P, As, and Sb, organic compounds of S,H,S, HCN, and polymerizing compounds such as vinyl acetylene. Such a catalyst shows a tendency to over-hydrogenate and produces tars, cuprene, polymers and other undesirable by-products. As high as 30 to 40% of organic matter has been found in such catalysts. Thus, repeated regeneration is necessary, with resultant catalyst loss and the tendency of the silica gel to glaze and lose its active surface. It has also been suggested to use catalyst of palladium containing other metals, e.g. 10% cobalt or nickel; or to use platinum instead of palladium. In addition, catalysts of nickel-silver have been tried, but a really good commercially feasible selective catalyst for this purpose has not previously been suggested. In every case there is a considerable tar formation in addition to ethylene.

There is thus a need for a catalyst capable of selectively hydrogenating acetylene in the presence of other gases, particularly olefines, wherein the acetylene content must be effectively eliminated or reduced to only tiny amounts, and not more than1% of any ethylene present is converted to ethane.

It is therefore one object of the present invention to provide a catalytic process for the hydrogenation of the triple bond of acetylene. It is a furrher object of the invention to provide a catalytic process for the selective hydrogenation of even traces of acetylene to ethylene when the acetylene is present in a mixture with saturated and unsaturated gases. A still further object is to provide a simple and economical catalytic process for the selective hydrogenation of acetylene to ethylene when the acetylene is present in traces in a mixture with olefines.

Other objects and advantages of the invention will become readily apparent from the following description.

We, have now determined that selective hydrogenation of acetylene,wherein the acetylene is present in a mixture with other gases, both saturated and unsaturated can be effectively brought about with alad catalyst on an activated alumina carrier. and without materially changing the otherunsaturatcd hydrocarbons present in such gaseous mixtures.

Thus the Pd catalyst used in the process of the invention has been found to be practically inactive for the double blond while being still active for the triple bond. To accomplish this desired object, we have found that the Pd content is very critical. The Pd-alumina catalyst used has proved to be superior to otherknown Pd catalysts and operates on higher space velocities and lower temperatures and is selective over a wide range of temperatures.

Because of its selectivity and operability at low temperatures the catalyst of this invention does not promote the "run-away" exothermic reaction occurring where theC2H4 constitutes20%30% of the gas and a large amount of hydrogen is present (i.e. the formation of ethane from ethylene evolving sufficient heat to increase the rate of ethane formation). We have found that the more H2 present in the gas to be hydrogenated, the lower the Pd content should be. The Pd content of the catalyst should be within the range of0.001-0.035 %.

As stated above, the catalyst is Pd on activated alumina with a specific small range of Pd content. However, the catalysts also contain other catalytic metals which do not interfere with the selective catalytic effect of the palladium The presence of small amounts of these other metals acting as promoters, as specified hereinafter, greatly improves the effectiveness of the catalyst. The catalysts have been found to be operable at elevated pressures.

Maintaining a certain temperature range is advantageous.

As to the above mentioned presence of promoter metal in the activated aluminapalladium catalyst, it has been found that certain metals, when used in certain critical ratios, are useful as promoters for the catalyst metal palladium in the selective hydrogenationof acetylene in hydrocarbon gaseous mixtures when palladium and the promoter metal in specific proportions are supported on the activated alumina support. As a result, maximum selectivity of palladium results at higher proportions by weight of palladium without increasing the relative rate of polymeric buildup. As a consequence, catalyst regeneration can be accomplished without affecting the palladium content of the catalyst to the extent of interfering with its high selectivity.

More specifically, it has been found that the metals Rh, Ag and Fe, when used in certain proportions by weight, improve the selectivity of the palladium in the hydrogenation of hydrocarbon mixtures containing acetylene in amounts up to about 2 per cent by weight. The palladium content of the catalyst of the present invention ranges as said above from 0.001 per cent to 0.035 per cent by weight of the total catalyst. Preferably for the purpose of improved regeneration without loss of activity the range is from about 0.007 per cent to about 0.035 per cent. The promoter metals should be present in amounts ranging from 0.001 per cent to 5 per cent by weight of the catalyst i.e. of the total weight of palladium, activated alumina and promoter metal.

The catalysts are conveniently prepared by forming an aqueous solution of a salt of palladium and an aqueous solution of a salt of the promoter metal and contacting the carrier in the form of a dehydrated solid, e.g. anhydrous oxide of aluminumwhich is insoluble in water, with the solutions to permit the salts to form a firm and adherent deposit of oxide or hydroxide on the surface of the carrier. The resulting material is subsequently reduced to obtain the active catalyst. If desired, a combined solution of salts of palladium and the promoter metal may be used in place of separate solutions.

In accordance with certain preferred embodiments, certain of the promoter metals are found to be particularly efficient in aiding in the catalytic hydrogenation of certain gaseous hydrocarbon mixtures by the catalyst according to the invention. It is well recognised that a particular gaseous hydrocarbon mixture necessitates a specific catalyst in order to obtain optimum results.Srated differently, a catalyst of unusually high selectivity for the hydrogenation of a given hydrocarbon mixture may not be as effective as another catalyst of slightly different proportions by weight or differing composition for catalyzing the hydrogenation of another given hydrocarbon mixture.

In general, it may be stated that a small acetylene content of a hydrocarbon mixture containing up to about 2 per cent by weight of acetylene together with a balance consisting substantially of ethylene and ethane is most effectively hydrogenated in accordance with the preset invention when the catalyst consists of palladium and as promoter rhodium, sup ported on the activated alumina carrier. A highly effective catalyst contains about 0.01 per cent by weight of palladium and about 0.01 per cent by weight of rhodium. Hydrocarbon mixtures consisting essentially of up to 2 per cent by weight of acetylene and a balance consisting substantially of ethylene and ethane are commonly referred to as "commercial ethylene". Typical analyses of commercial ethylene are as follows:
A.C2H2-0.005-2 per cent
C2H4-90-99.9 per cent
C2H6, CH40. 1-4 per cent B. C2H2-0.005-2 per cent
C2H4-20-80 per cent C2H-balance
In the event that the gaseous hydrocarbon mixture consists essentially of up to about 2 per cent by weight of acetylene and a mixture of hydrocarbons including hydrocarbons of higher molecular weight than ethane, for example, a mixture of the following composition:
C.C2H2-0.05-1 per cent
C2H4-15-35 per cent
C2H6-5-15 per cent
H2-10-35 per cent
CH4,C2Hc, Cub,, CH1,--balance a preferred catalyst has been found, in accordance with the present invention, to be one consisting essentially of palladium and silver as promoter metal, supported on activated alumina. For this type of mixture, a highly effective catalyst contains about 0.01 per cent palladium and about 0.01 per cent silver based on the weight of the catalyst.

In accordance with the process of the present invention selective hydrogenation of hydrocarbon mixtures containing up to about 2 per cent of acetylene is accomplished as described in the beginning of the specification, by passing the gaseous mixture together with hydrogen in a quantity at least stoichiometrically equivalent to the acetylene content of the gaseous mixture over the catalyst at elevated temperatures and pressure conditions. To control temperature and pressure conditions, per se was known in the process of selectively hydrogenating acetylene in gaseous mixtures using other catalysts. The preferred conditions in a method applying the catalysts according to the present invention include a temperature within the range from 85 to 1650 C. and a pressure of from250lt50 psig. Space velocities of from about 3,000 to 7,000 volumes of gaseous mixture at normal pressure and temperature conditions per volume of catalyst per hour are found to be suitable to obtain an effluent containing not more than 10 ppm.

of acetylene. Regeneration of the catalyst upon accumulation ofpolymeric deposit may be accomplished by heating the catalyst in air at a temperature of, for example,5000 C. without substantial effect on the selectivity of the catalyst.

The following specific examples are for the purpose of illustrating the invention.

EXAMPLE I

Commercial ethylene (99 per cent ethylene and 0.25 per cent acetylene by weight) with an addition of about 0.7 per cent by weight of hydrogen was passed over a 0.01 per cent palladium and 0.01 per cent rhodium-containing catalyst supported on cylindrical 1/8" activated alumina pellets at a temperature of10e1400 C. under 350 psig and a space velocity of 5000 volumes of gas mixture (NTP) per volume of catalyst per hour. The effluent contained from 1 to 10 ppm.G,Hz and essentially no H2 after 200 hours. The catalyst was then regenerated by heating with air at 5000 C. Another gaseous mixture of the same composition was passed over the regenerated catalyst for800 hours, the effluent containing below 10 ppmC2H2.

EXAMPLE II

A gaseous mixture containing 33 mol per cent ethane, 66 mol per cent ethylene, 0.35 mol per cent acetylene, and 1.1 mol per cent

H2 was passed at a pressure of 350 psig. and a space velocity of 5000 volumes gas mixture (NTP) per volume of catalyst per hour over a 0.01 per centpalladium +0.01 per cent rhodium-containing catalyst supported on 1/8" activated alumina pellets, which had been previously heated to 5000 C. in air at a temperature of 1100 C. After 157 hours operation, the effluent still contained less than 5 ppm.Coy2.

EXAMPLE III

A gaseous mixture containing 34 per cent

H2, 33 per cent ethylene, 33 per cent ethane, 0.5 per cent acetylene by weight and traces of paraffinic compounds was passed at 90 liters per hour (NTP) over 20 grams of 0.005 per cent palladium and 1 per cent silver-containing catalyst supported on 1/8" activated alumina pellets at a temperature of130--1500 C. and a pressure of 35 psig. The effluent contained31.8-33 per cent H2. No acetylene was detected in the effluent gas.

EXAMPLE IV

A gaseous mixture containing, by volume, 15 per cent hydrogen, 26 per cent ethylene, 14 per cent propylene and 0.5 per cent acetylene was passed over a catalyst consisting of 0.01 per cent palladium and 0.1 per cent silver on 1/8" activated alumina pellets. The operating temperature was 1800 C. and the space velocity used was 5,000 volumes lof gasFer catalyst volume per hour. The acetylene in the effluent gas was reduced to less than 10ppn., and only a small amount of hydrogen was lost. after an initial catalyst seasoning period, which means that little ethylene was hydrogenated and the catalyst possessed good selectivity.

When the catalyst is spent, it can be regenerated by treatment with a mixture of air and steam for a period of about 2 to 6 hours at a temperature of about 400 to 5000 C., after which effective acetylene removal from the gas stream can be resumed.

WHAT WE CLAIMIS:-

1. A process for selectively hydrogenating acetylene in a gaseous hydrocarbon mixture containing up to about 2% by weight of acetylene, which process comprises passing the gaseous mixture together with hydrogen in a quantity at least stoichiometrically equivalent to the acetylene content of the gaseous mixture over a catalyst at elevated temeperature and pressure conditions, wherein the catalyst comprises palladium, a promoter metal selected from rhodium, silver and iron, and, as a carrier for the palladium and promoter metal, activatedalumina, the palladium being present in the range of from0.001% to0.035% by

WARNING end of DESC field may overlap start of CLMS **.

Catalytic hydrogenation of acetylene

Claims of **GB811820**

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per cent by weight of acetylene and a mixture of hydrocarbons including hydrocarbons of higher molecular weight than ethane, for example, a mixture of the following composition:
C.C2H2-0.05-1 per cent
C2H4-15-35 per cent
C2H6-5-15 per cent
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weight of the total catalyst and the promoter metal being present in the range of from0.001% to 5% by weight of the total catalyst

2. A process according to claim 1, wherein the temperature is in the range of from830 to 1650 C. and the pressure is in the range of from 250two 430 psig.

3. A process according to claim 1 or 2, in which the promoter metal is rhodium or silver, and in which the palladium and the promoter metal are each present in an amount equal to about0.01 % of the total weight of the catalyst.